STUDIES OF REMOVAL AND RECOVERY OF PALLADIUM FROM CHLORIDE MEDIA VIA AN ELECTROGENERATIVE SYSTEM

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by

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LIST OF SYMBOLS AND ABBREVIATIONS

$\Delta G°$	standard free energy, kJ mol^{-1}
A	area of electrode, cm^2
A_e	the specific surface area of the cathode, m^{-1}
A_s	active electrode area per unit reactor volume, m^{-1}
C_0	initial concentration of the operation, mol cm^{-3}
C_t	concentration of the metallic ion as a function of operation time t, mol cm^{-3}
$E°$	standard reduction potential, V
$E°_{cell}$	overall cell potential, V
F	Faraday's constant, 96485.309 C mol^{-1}
k_m	mass transfer coefficient, m s^{-1}
n	number of mole of reactant
ppi	pores per inch
R_b	bulk resistance, Ω
t	time, s
t	thickness of the electrode, cm
V_e	catholyte volume, m^3
V_R	the total volume of catholyte in the cell, m^3
σ	conductivity, $(\Omega\ cm)^{-1}$

KAJIAN PENYINGKIRAN DAN PEROLEHAN SEMULA PALADIUM DARIPADA LARUTAN KLORIDA MELALUI SISTEM ELEKTROGENERATIF

ABSTRAK

Penggunaan paladium pada masa kini adalah meluas terutamanya sebagai penukar bermangkin kenderaan yang menyumbang kepada peningkatan permintaan setiap tahun. Dengan sumber yang terhad dan kos yang tinggi dalam proses perlombongan dan penulenan, paladium telah dikitar semula oleh pihak industri. Namun begitu, logam berharga ini sukar dan memerlukan kos tinggi untuk dirawat terutama bagi kepekatan yang rendah (<500 mg L^{-1}). Untuk mengatasi masalah ini, sistem elektrogeneratif telah diperkenalkan untuk peroleh semula paladium dalam larutan klorida. Sistem ini adalah kaedah alternatif bagi kaedah elektrokimia yang lain dimana tindak balas kimia berlaku secara spontan kerana tidak memerlukan sebarang bekalan tenaga luar. Sel kelompok statik telah dibentuk untuk merawat paladium berkepekatan rendah dalam larutan cair. Larutan klorida yang cair dengan kepekatan 0.1- 0.2 M NaCl adalah optimum untuk merawat paladium dengan kepekatan 100-500 mg L^{-1}. Bahan katod tiga-dimensi karbon kaca berongga (RVC) yang dirawat dengan asid sulfurik memberikan prestasi terbaik untuk pemendapan paladium yang optimum. RVC didapati mempunyai rintangan rendah dan kadar pemindahan jisim yang tinggi dari analisis sokongan menggunakan spektroskopi impedans elektrokimia dan voltammetri berkitar. Aliran arus yang dihasilkan sistem ini disokong dengan zink sebagai anod. Keseluruhannya, sistem ini menunjukkan kira-kira >90% paladium telah diperoleh semula dalam 6 jam operasi. Pemendapan paladium pada katod RVC dapat dilihat dengan mata kasar dan telah dibuktikan dengan analisis selanjutnya

menggunakan mikroskopi elektron pengimbas-spektrometri penyerakan tenaga sinar-X.

STUDIES OF REMOVAL AND RECOVERY OF PALLADIUM FROM CHLORIDE MEDIA VIA AN ELECTROGENERATIVE SYSTEM

ABSTRACT

The use of palladium nowadays is extensive especially as catalytic converter of vehicles which contributed to increasing demand every year. With the limited source and higher cost in mining and purifying process, palladium is recycled by the industries. However, this precious metal is difficult and required high cost to be treated especially in such low concentration (<500 mg L^{-1}). To overcome this problem, an electrogenerative system was introduced to recover palladium in chloride medium. It is alternative method to other electrochemical methods where the chemical reaction takes place spontaneously in this system since it does not require any external supply of energy. A static batch cell was set up to treat low concentration of palladium in dilute solutions. The dilute chloride with the concentration of 0.1-0.2 M NaCl was optimum to treat palladium with concentration 100-500 mg L^{-1}. A three-dimensional cathode material of reticulated vitreous carbon (RVC) treated with sulphuric acid appeared to give the best performance for optimum palladium deposition. The RVC was found to have low resistance and high mass transfer from supporting analysis using electrochemical impedance spectroscopy and cyclic voltammetry. The generated flow current in this system was supported with a zinc as an anode. Overall, this system showed about >90% of palladium being recovered within 6 h of operation. The reduction of palladium ion was proved by controlled potential using cyclic voltammetry. The deposited palladium on the cathode RVC is visible with naked eyes and was further confirmed by the scanning electron microscopy-energy dispersive X-ray spectroscopy.

CHAPTER 1 INTRODUCTION

Metal recovery has been used throughout the world usually from a secondary source such as the effluent of the industry since the awareness of limited natural resources. When it comes to industrial usage, it is important to develop an effective and efficient chemical processes method. In addition, many industrial chemical processes involve an exothermic process which generates a sum of heat waste. These heat, are often not recovered or removed since the cost is quite high. An alternative process, which is on the electrogenerative system can be applied in order to recover and manage the waste as well as a potential application for metal recovery.

1.1 Background research

A recovery metal process is not new process in recycling industry. In order to achieve the high purity of metals in the end of this process, electrocatalytic method was chosen in many industries in the past few years because it was selective to the desired metal depending on the control of the current in the cell. This method is a type of electrochemical method which offers efficient and environmentally acceptable in metal refining and recycling. It is the most utilized method and it is known as hydrometallurgy. Hydrometallurgy is a method consist a few steps which suitable for a big production in industry since it can deal with a large quantity of metal scrap in a short period of time. However, this method has a drawback in the treatment of dilute solution. In dilute solutions (1 to 1000 mg L^{-1}), the current efficiency is very low due to the side reactions occurring in the system. Thus, the power consumption in treating dilute solution is rather high and not cost effective.

The other type of electrochemical method is called a galvanic process which is different from an electrolytic process in the term of the current applies. What interesting about the galvanic process is that it only depends on the energy generated by the chemical energy occur from a spontaneous reaction in the solution itself. Hence, it can be an alternative for the less usage of high power consumption in order to trigger the chemical reaction. An electrogenerative process which the driving mechanisms depend on the spontaneous redox reaction, does not used any external power source. The other advantage of this process is that it is suitable for the treatment for low metal ion concentration.

One of the precious metal which recently getting important in recycling industries is palladium, Pd. Pd is a rare precious metal from platinum group metal (PGM) which excessively used in chemical processes as catalyst especially in vehicles. The use of Pd in the vehicle is at the part called catalytic converter which functions to reduce the emission of toxic gas from the exhaust. Pd has the major concentration in the catalytic converter of gasoline fueled vehicles (up to 5 g Pd per litre catalyst volume) replacing the platinum mainly due to Pd's relatively lower cost and better performance in autocatalysts (Zereini & Alt, 2011). Meanwhile, the production of vehicle is rising every year, the allowable emissions standards and legislation also become stricter, automatically affected the demand of Pd.

1.2 Problem statement

The metal recycling method could reduce the dependency of sourcing metal from earth crust and it is also economical. The major concern on Pd is that the unbalance between the higher demand and the limited source since the production of cars are increasing over the years. Since the PGM are very expensive to mine and purify, a high proportion of them are recycled by the metal recycling industries. Since the current technologies involve large amount of metals and chemicals, a large amount of power is required to complete the process. Besides, waste treatment is also costly. In order to meet the standard waste to be released to the landfill, it is almost impossible to the current technologies recover to the finest amount to even less than 500 mg L^{-1}. This waste will accumulate and give a bad effect to the environment.

Towards the environmentally friendly technology to recover Pd in a dilute solution, a new system was innovated in purpose of to overcome this problem. An electrogenerative batch cell can be a new recovery system highlights the advantage which it can generate its own electricity. Besides, it has a simple setup and operation, cost effective and use minimal reagents. This system is considered economical and can recovered even less than 500 mg $L^{-1.}$

Moreover, the use of chloride aqueous medium fulfills the tendencies for clean technology without disposal of waste since chlorine can be recovered as a gas and less hazardous than cyanide. Thus, the optimum condition of the recovery of Pd in a chloride media via an electrogenerative process will be determined in this project.

1.3 Objectives of research

As the benefits which have been discussed, the electrogenerative process is chosen to investigate and identify improved means for carrying out Pd recovery with an electrogenerative system.

The objectives of this research are summarized as the following:

i. To study the deposition of Pd from a chloride medium by using an electrogenerative process.
ii. To determine the optimize Pd recovery condition on batch cell setup.
iii. To investigate the suitable cathode potential for the Pd recovery process in the batch cell.
iv. To examine the effect of different electrodes configuration in Pd recovery process.

In this project, an electrogenerative process was used as an alternative to the more expensive and complicated electrolytic recovery processes such as hydrometallurgy and electrocatalytic method. An electrogenerative batch cell was used in this present work because it is economical and most suitable for handling small volume and concentration. Few parameters were tested to evaluate the performance of the batch cell system which is the type of electrode used in the cell, the effect of pre-treatment on the cathode, the initial concentration of Pd, the concentration of the medium use, the effect of supporting electrolyte and influence of pH. The thermodynamic, kinetic and mass transport characteristics of the chloride system were further explored in order to optimize the Pd recovery. Finally, the surface morphology and composition of Pd deposits were also investigated.

CHAPTER 2 LITERATURE REVIEW

This chapter is divided into two categories, i) technologies related to Pd recovery studies and ii) studies on the electrogenerative system. Recovery of Pd is reviewed in the first part of this chapter. A few important preparations related to the electrogenerative system is discussed in the second part of this chapter.

2.1 Palladium (Pd)

Pd is a precious silver-white metal which widely discovered in the field of catalysts due to its efficiency. Ever since the motor vehicles first introduced, Pd has been used as exhaust emission catalysts or a catalytic converter for the treatment of pollutants in exhaust gases. The catalytic converter oxidizes carbon monoxide and hydrocarbons into carbon dioxide and water, using platinum and Pd while rhodium reduces nitrogen oxides to nitrogen. Until now, Pd is widely demanded and used in other various purposes from electronics and electrical devices, jewelry, dental alloys to a medical application like glucose monitoring machine and even in the treatment for cancer (Fernandes et al., 2016; Pat-Espadas et al., 2015).

Pd has attractive properties such as resistance to chemical corrosion over a wide temperature range, high melting point, high mechanical strength, and good ductility, reasons for which they are extensively used in industrial processes. Pd has been of interest as a partial substitute for gold in some electronic application and jewelry. Besides, in the past few years, Pd has been the replacement of platinum in gasoline catalysts since Pd results in better performances and economic advantage compared to platinum. (Iavicoli et al., 2011; Zereini & Alt, 2011)

Currently, the world supply for Pd is contributed mainly from South Africa and Russia, while minor productions derive from Zimbabwe, North America, and Philippines. The average content in the principal mining sites spans between 2 and 20 g t^{-1}. In contrast, generally, the automotive catalytic converters contain about 150 g t^{-1} while some electronic wastes such as the printed circuit boards contain up to 100 g t^{-1} (Di Natale et al., 2017). Therefore, an effort must be taken to make the balance between the demand and supply from natural resources.

After a certain period of active life, these potential secondary sources like catalysts and the electric and electronic equipment will get deactivated. At this stage, it is going to be considered as a waste (Reddy et al., 2010). These waste especially spent catalysts are harmful to the environment because of the presence of soluble/leachable organic and inorganic compounds. Furthermore, the policies on their disposal into the landfills is also restricted. Hence, on the basis of environmental protections as well as resource saving, Pd need to be recovered and recycled from secondary sources.

2.1.1 Treatment technologies for Pd recovery

Many years ago, the study of metals recovery especially Pd already taken place. Different methods to recover Pd from aqueous solutions are used by industries such as solvent extraction, ion exchange and electrochemical methods. Depending on the method applied, there are significant differences in the reaction conditions. However, these methods have their own benefits and drawbacks, depending on the type of waste involve such as from ore mining, electronic scrap, leachate liquor or spent waste.

The traditional technology in recovering Pd is called pyrometallurgy. Generally, it is a method for recovery of precious metals and it involves extraction and purification of metals by processes involving the application of heat. In this process, the crushed scraps are burned in a furnace or in a molten bath to extract the precious metals. However, the energy must be added to the high temperature process either by combustion of fuel or by direct external power which results in high power consumption. Besides, few drawbacks like the formation of toxic gas from the presence of halogenated flame retardants and long process time to extract the precious metal are need to be improved (Cui & Zhang, 2008).

Compare to pyrometallurgy, hydrometallurgy method has been more extensively studied and used since it is an environmentally friendly method (Choudhary et al., 2017). Hydrometallurgy is the other type of extracting metals process which involves dissolution processes of metals by an aqueous solution. The dissolution processes could be a leaching or a separation process or combination of both processes. The most common leaching agents used in the recovery of Pd include cyanide, aqua regia, hydrochloric acid, nitric acid and sulfuric acid in the presence of additives like oxygen, iodine, chlorine and hydrogen peroxide which results in leach liquors (Paiva et al., 2017). However, hydrometallurgy process requires a large amount of reagents and the high cost for waste treatment (Barakat et al., 2006; Dong et al., 2015).

Solvent extraction is a common method being applied in many research for the purpose of treating domestic and industrial effluents. It is capable of promoting a successful separation of Pd by selecting a suitable extractant such as quarternary salts, amine, thiourea, and oxime (Cieszynska & Wiśniewski, 2012; Dakshinamoorthy et al., 2008; Lee et al., 2010; Reddy et al., 2010). Due to its simplicity of tools and operations,

solvent extraction or liquid-liquid extraction is widely used for separation process in the nuclear industry and chloride leach liquor of spent catalyst (Paiva et al., 2017). Besides, a complete removal of metals is possible through the use of multi-stage extraction (Reddy et al., 2010). However, the extraction rates of the metals are generally low and a large amount of extractants and solvents were required to make up the separation (Kakoi et al., 1996).

Next technique is ion exchange method which involves a solid that is capable to exchange either cations or anions with surrounding materials. In most studies, resins are used due to its good capacity for adsorption. Various types of resins are used in the removal of Pd ions. Usually, they have large ion-exchange capacities, which allow metals to be adsorbed extensively. Their capacity, however, mainly depends on the type and the quantity of active functional groups such as thiol, thiourea, melamine, formaldehyde and tertiary amine (Birinci et al., 2009; Hubicki et al., 2007; Hubicki & Wolowicz, 2009, Hubicki et al., 2009). These functional groups which contain one or more donor atoms are capable to form complexes directly with metal ions (Birinci et al., 2009). However, resins cannot handle the concentrated metal solution as they are easily get contaminated by organics and other solids in the wastewater (Barakat, 2011).

Adsorption was another technique for treating domestic and industrial effluents which involve transport of ions from the liquid phase to the surface of a solid (Barakat, 2011). Recently, biosorption method has been widely studied. Natural biomasses such as drop fruits residues, fruits stalk, tannins and biomaterial such as algae, bacteria, and granular sludge (Choudhary et al., 2017; Ju et al., 2016; Mavhungu et al., 2013; Pat-Espadas et al., 2016; Yi et al., 2016; Yong et al., 2002) have the adsorptive capacity to bind with Pd in the waste residue. This method is easily available, eco-friendly, low-cost, produces much less toxic waste and have high efficiency in detoxifying effluents

(Choudhary et al., 2017; Das, 2010). However, microbial biomass suffers from drawbacks such as difficulties in solid-liquid separation owing to small particle size, low density, poor mechanical strength and low reusability (Gadd, 2009).

An electrochemical method especially the electrolytic method is one of technology to recover metals which uses electricity to pass a current with the aid of a pair of electrode through an aqueous solution (Barakat, 2011). Electrowinning is commonly used as the final step in the hydrometallurgical method for pure metal recovery. Specific metals will be deposited on cathode usually stainless steel before scrubbing step to collect high metal purity. The choice of the electrode was a crucial part in this method to ensure redox reaction to occur in order to achieve the deposition of metal. In fact, other types of cathodes were also widely used in electrodeposition studies to recover Pd such as gold, platinum, glassy carbon, and graphite (Danaee, 2011; Liu et al., 2013; Li et al., 1997; Quayum et al., 2002).

The cell design with a few important cell compartments is another crucial part of the electrolytic method. As for instance, Terrazas-Rodríguez et al., (2011) reported the catalytic deposition using rotating cylinder electrode reactor (RCER) is better than a parallel plate reactor in term of deposition time due to the presence of microturbulances in RCER which favors high mass transport. The electrolytic method is a simple, cost effective, generate less secondary waste besides the ease of direct reduction to metals and does not demand the addition of external reagents (Kumaresan et al., 2014; Liu et al., 2013).

2.2 Electrogenerative system

An electrogenerative system is an electrochemical process which results in the reduction of metal ions to elemental metal at the cathode. Similar to a galvanic system, the energy associated with chemical reactions is converted into an electrical energy or a direct current electricity as a by-product. Fuel cell processes are related to electrochemical and galvanic system category but it generally highlights a complete fuel combustion and maximum electrical energy production with little or even no consideration given to recover the products.

Although electrogenerative systems and fuel systems are to share the use of catalytic electrodes even the cell components itself, they are different in their main function. The chemical processing features have created special considerations in electrogenerative process such as product recovery, hence, the specific designation for this type of system is considered. Therefore, this process, with a combination of favourable thermodynamics and the kinetic factors, will produce or remove the desired chemical and to generate direct current (DC) between matched electrodes in an electrochemical cell arrangement (Langer, 1992).

The most interesting characteristic of this system which different from the electrolytic system is that it does not require an external source energy due to the spontaneous chemical reaction that takes place in the operation. In order to carry out a spontaneous reaction, the suitable couple of electrodes and electrolytes must be identified hence, a direct current will produce as a by-product. During the operation, an electrode with high positive standard reduction potential shows a strong tendency towards reduction (gain electrons) or simply known as a cathode, in contrast, an anode which has lower standard reduction potential will undergo oxidation (lose electrons).

For a reversible electrochemical cell, the thermodynamics can be described by Gibb's free energy:

$$\Delta G^\circ = -nFE^\circ_{cell} \quad (1.1)$$

where n is the number of mole of reactant, F is Faraday's constant and E°_{cell} is the overall cell potential. The spontaneous chemical reaction occur in an electrogenerative system will give a negative value of standard free energy, ΔG° in overall reaction as the reactants and products are at their standard states, usually 25℃ and 1 atm. The negative value represents the release of energy during the operation.

In electrochemical systems, the electrodes act as a conductor and a contacting sample solution is called electrolyte. The electrode surface performs as a junction between an ionic conductor and an electronic conductor. The reaction of the electrode has made the interest in kinetic factor as it involves a few contributed process: (1) the reactant or electroactive species diffuses from bulk solution to the electrode surface, termed mass transport, (2) redox chemical reaction which involve the electron transfer across the electrode surface encourages the potential difference and (3) mass transport of product from surface to bulk solution. A schematic representation of the electrode reaction shown in Figure 2.1.

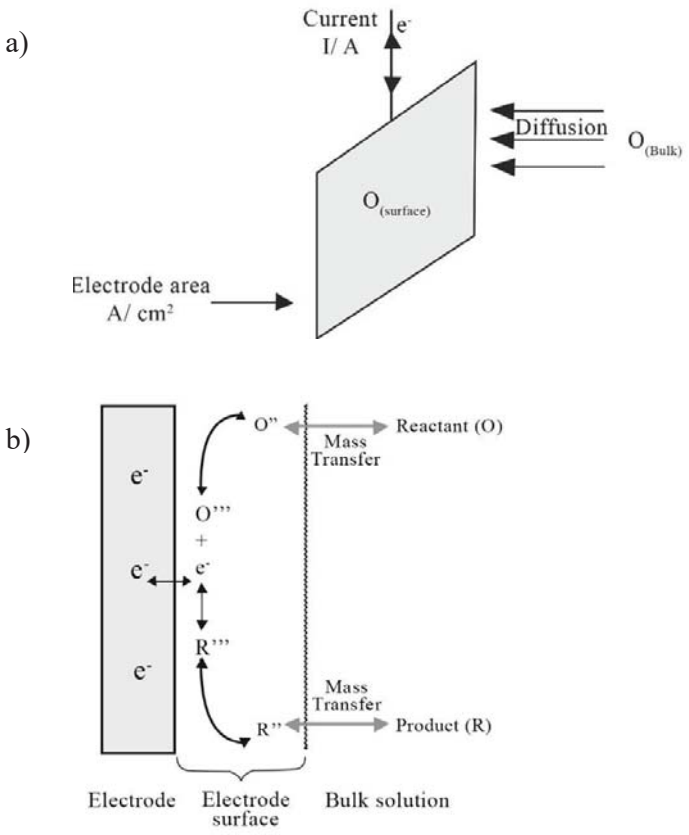


Figure 2.1 (a) A simple electrode reaction and (b) The general electrochemical reaction pathway (Adopted from Brownson & Banks, 2014).

The general electrochemical process shows that the observed electrode current is dependent upon mass transport. In these processes, the substances consumed or formed during the electrode reaction are transported from the bulk solution to the interphase (electrode surface) and from the interphase to the bulk solution. Mass transfer mostly occurs via diffusion mode. Diffusion by means, the spontaneous movement under the influence of the concentration gradient, from regions of high concentrations to regions of lower ones. The mass transport usually becomes dominant consideration which can be investigated by measuring the current density at a potential where the electron transfer reaction is very fast.

The electrons involve during redox reaction will usually be collected by an electrode. Electron transfer as mentioned during the electrode reaction can be described into two classes which are homogeneous and heterogeneous electron transfer. The homogeneous reaction involves the transfer of an electron between the two molecules in the solution (liquid) and the difference in energy levels is the driving force for the reaction. While the heterogeneous reaction is when the electroactive material is in solution (liquid) and is electromodified at an electrode (solid) which exists as a separate phase. Usually, through an external power source, the voltage can be applied to the electrode to control the energy of the electron in the electrode. Figure 2.2 below presents the visual example of electron transfer.

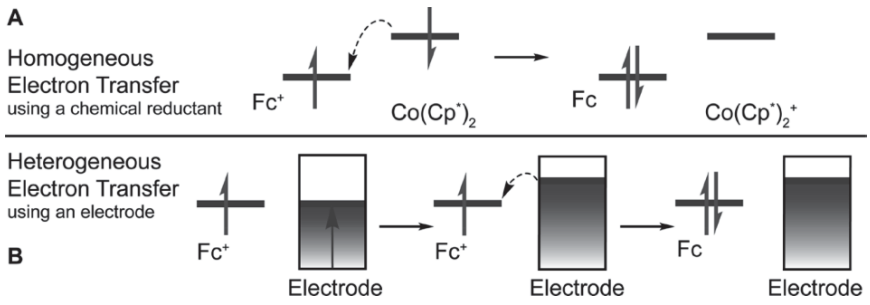


Figure 2.2 Schematic diagram of an example in electron transfer reaction (Adopted from Elgrishi et al., 2018).

2.2.1 Studies of electrogenerative system in different metals

A concept similar to electrowinning, electrogenerative process was developed as an alternative metal recovery technique. Using the same key concept of the electrochemical method which is a couple of electrodes, electrolyte and a complete circuit, an electrogenerative is a galvanic process and offers a low cost process compared to an electrowinning process since it can generate its own electricity.

Studies on metals recovery using an electrogenerative process have been proven with the application of flow through cells and batch cells. A simple batch reactor has given promising results in the treatment of dilute simulated metal solutions (Min et al., 2013; Ramalan et al., 2012). In addition, a 3-dimensional (3D) RVC has been reported to be superior cathode in for various metal deposition such as gold, cobalt and lead. A batch cell reactor was reported to achieve more than 99% of gold recovery in from a cyanide solution (Yap & Mohamed, 2007) and a chloride solution (Karoonian et al., 2012; Roslan et al., 2017a). An application of the flow-through reactor was reported by Roslan et al., (2017b) to recover gold from E-waste. More than 99% of gold was recovered within 2 h using a single flow cell compared to few flow cells in series which recovered 98% gold in 4 h of operation. Other metals recovery process like lead (Ramalan et al., 2012) and cobalt (Min et al., 2013) were also reported using a batch cell with more than 90% of metal recovery without using an external power supply. An electrogenerative method promises an economically attractive treatment system because of its low operational cost and reduce reagents consumption.

As an alternative to metal waste treatment technologies, an electrogenerative process gives a promising potential for easy and cost-effective method in metal recovery especially for noble metal like Pd. However, there is no literature has been reported on the recovery of Pd using an electrogenerative process.

2.2.2 Important parameters related to an electrogenerative system

A good cell design contributes to the accomplishment of Pd recovery using an electrogenerative system. The preparation is crucial to each different design of the system. Each of the modification gives big changes in the work. In contrast with the previous work on electrogenerative studies discussed in Section 2.2.1, experimental procedure for the recovery of Pd requires some changes depending on the nature of the metal itself. Few highlighted factors such as choice of electrode, type of medium and type of ion exchange membrane in this system were discussed below.

2.2.2(a) Choice of cathode

The choice of working electrode is very important in this project where the deposition will take place in the recovery process. The electrode was coupled with suitable anode and immersed into an electrolyte containing electroactive species or catholyte with a supporting electrolyte salt to achieve high conductivity. Carbon is one of material which is usually available and has been a natural choice especially in fuel cell industries (Maniam et al., 2014). Some 3D electrodes like a fluidized bed, packed bed or a porous material have counteracted the limitations of low space-time yield in 2-dimensional (2D) electrodes (Friedrich et al., 2004). Furthermore, they have found that the RVC with attractive characteristics such as microporous honeycomb structure and glassy carbon electrode material, has a potential of new electrochemical cell designs with its benefits. For not only having a high corrosion resistance with good porosity high surface area, RVC offers high current densities, low electrical resistance and high electrical conductivities as an electrode. From previous work based on electrogenerative for recovery of metals, over 90% metals of gold, cobalt and lead were recovered using RVC (Min et al., 2013; Ramalan et al., 2012; Roslan et al., 2017a;

Yap & Mohamed, 2007). Hence, it was proved that 3D RVC was superior as a cathode in depositing metals compared to 2D electrodes like graphite and stainless steel.

It is interesting to mention that there is no report on the use of an electrogenerative process for recovery of Pd up to date. Electrochemical recovery of Pd was only been carried out by an electrodeposition process. By using electrodeposition process, the desired metal can be selectively recovered but it depends on the cathode potential applied to the electrode.

Li et al., (1997) have used a glassy carbon electrode and found Pd complex formation through coordination to the oxygen atom of the oxide functional group on the pretreated glassy carbon electrode through electrodepositing highly dispersed in the sulfuric acid solution. The electrode was then had almost completely transformed to Pd after undergoes electroreduction using cyclic voltammogram. Danaee (2011) studied the nucleation and growth of Pd through electrodeposition by cyclic voltammogram onto graphite electrode from the alkaline bath. While Jayakumar et al., (2007) reported a Pd deposit on a 2D stainless steel electrode with controlled potential through electrowinning from the solution of the ionic liquid. The morphological analysis revealed that the deposition of Pd occurs through dendrite formation at different potentials after nucleation.

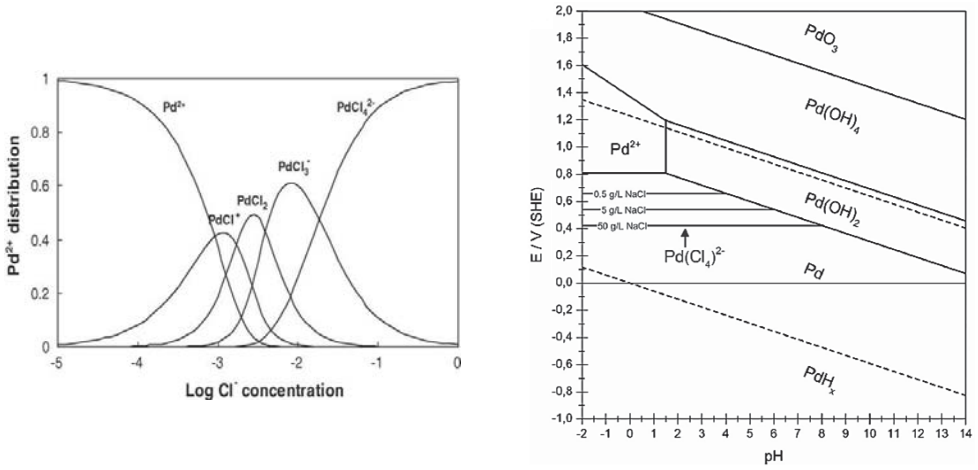
Meanwhile, the electrogenerative processes can be made selective for particular reactions by the choice of electrodes used for the system. Various types of electrodes including the comparison between 2D and 3D cathodes structure will be investigated in this work and further discussion about their influence on the recovery process will be provided in Chapter 4.

2.2.2(b) Medium

Pd is frequently leached in aqua regia, cyanide and acids, such as sulfuric acid, hydrochloric acid and nitric acid. Liu et al., (2013) studied the electrowinning of Pd from nitric acid medium and reported substantial Pd deposition occurs in a wide range of nitric acid. However, concentrated nitric acid was reported to cause an environmental pollution and it is not favorable due to the high cost of the acid and may evolved to form hazardous nitric oxides (Barakat et al., 2006). Jayakumar et al., (2009) reported the use of ionic liquid in electrodeposition to separate Pd from simulated HLLW with controlled potential using stainless steel as cathode and platinum as an anode. The use of ionic liquid as electrolyte is for non-aqueous reprocessing of spent nuclear fuel and as a substitute for high-temperature molten salts. However, the recovery of Pd reported was below 40% due to the competitive redox reactions from the presence of several interfering ions in HLLW.

Chloride solution has been reported widely in the extraction and recovery of metal since it gives high performances in refining steps in hydrometallurgy. In addition, it is a cost-effective medium which all the Platinum Group Metal (PGM) can be brought into solution as well as the ease of chlorine recycling by electrolysis of aqueous media (Bernardis, et al., 2005; Paiva et al., 2013; Szymanowski, 1996). Besides, chloride salts are non-toxic, stable and can enhance the formation of chloro-complexes of metals (Skrobian et al., 2005). As for the structure of the metal deposits, chloride able to refines the grain size of metal deposits (Winand., 1991; Yao., 1944). There is no report on the use of chloride media even in electrochemical for the recovery of Pd. Most of the Pd recovery in chloride media was reported using other method like solvent extraction and ion exchange (Hubicki and Wolowicz., 2009; Nikoloski et al., 2015; Paiva et al., 2013; Paiva et al., 2017).

In general, the effective complexing ions process in a solution made the dissolution of the metal to be possible. According to Barakat et al., (2006), depending on chloride concentration, the presence of chloride ions results in the formation of stable Pd chloro-complex ions as illustrated in Figure 2.3 (a) and most of the Pd chloro-complex ions lie within the water stability region (Figure 2.3 (b)). This formation will then lead to the increase of the metal reduction strength thus give the dissolution reaction to work (Barakat et al., 2006; Mahmoud, 2003).



(a) (b)

Figure 2.3 (a) The calculated distribution graph of Pd species in different chloride concentration (Barakat et al., 2006) and (b) Pourbaix diagram for Pd species at 25°C (Gerstl et al., 2015).

2.2.2(c) Ion exchange membrane

Ion exchange membranes were usually used in a process such as electrodialysis. The concept of electrodialysis involves the use of a selective ion membrane which positioned between a pair of electrodes and the flow of ions in solution was depend on applied voltage (Yap & Mohamed., 2008). Membrane properties such as the electrical resistance is crucial which can give a significant impact on the cell performance. Neosepta® membranes are widely studied and used especially in electrodialysis process. It was a homogeneous membrane which provide a good electrochemical property in term of low membrane resistance. The idea in the present work is to use an ion exchange membrane from Neosepta® for separation between two types of electrolyte in an electrogenerative batch cell. Długołęcki et al., (2010a) reported the characteristics of Neosepta® membrane in the concentration range of 0.01 to 0.5 M NaCl at 25 ^{o}C (Table 2.1).

Table 2.1 Neosepta® membrane characteristics (Długołęcki et al., 2010a).

Membrane	**Ion Exchange Capacity (meq. g^{-1})**	**Resistance (Ω cm^2)**	**Thickness (µm)**	**Properties**
AMX—anion exchange	1.25	2.35	134	High mechanical strength
CMX—cation exchange	1.62	2.91	164	High mechanical strength

2.2.3 Kinetic study of electrogenerative process

A porous 3D electrode can have a very high surface area as well as leading to more turbulent mass transport condition adjacent to the electrode surface in electrochemical approach. For 3D electrode like RVC and PG, a model of concentration-time relationship for a batch system can be expressed by Equation 2.1:

$$\ln\left[\frac{C_t}{C_0}\right] = -\frac{V_e}{V_R} k_m A_e \, t \tag{2.1}$$

where C_t is the concentration of the metallic ion as a function of operation time, C_0 is initial concentration of the operation, V_e is the catholyte volume, V_R is the total volume of catholyte in the cell, k_m is the mass transfer coefficient and A_e is the specific surface area of the cathode (Bertazzoli et al., 1997).

While for 2D electrode like stainless steel, $k_m A_e$ from Equation 2.1 was presented as $k_m A_s$. A_s represents the active electrode area per unit reactor volume as in Equation 2.2:

$$A_s = \frac{A}{V_R} \tag{2.2}$$

In the present work, the batch cell can put up until 100 mL electrolytes in each compartment. Thus, the V_e/V_R value would be 0.5 for all operation. From the slopes of ln C_t/C_0 vs time plot which represents the rate constant that involved in the recovery of Pd, $k_m A_e$ and $k_m A_s$ for each cathodes can be calculated.

CHAPTER 3 EXPERIMENTAL

3.1 Chemicals and materials

All solutions were prepared from analytical grade reagents which are palladium(II) chloride, $PdCl_2$ (R&M) (United Kingdom), Sodium chloride, NaCl (Bendosen) (Norway). The materials used throughout the experiment were ion exchange membrane Neosepta® AM-01 (Tokuyama Corp.) (Japan), electrodes such as RVC 80 porous per inch (ppi) (The Electrosynthesis Co.) (USA), porous graphite PG-25 (National Electrical Carbon Products, Inc.) (South Carolina), and stainless steel (R&M) (Malaysia), zinc foil (R&M) (United Kingdom), and aluminum foil (Malaysia). 1000 mg L^{-1} palladium standard solution (Merck) (Germany) was diluted to a few concentrations for sample concentration analysis.

3.2 Electrogenerative cell design

The electrogenerative batch cell was made of Plexiglass with two electrolyte compartments (5.5 cm × 5.5 cm × 8.0 cm each) separated by an anion exchange membrane. The schematic diagram of the cell is shown in Figure 3.1. The galvanic cell components were held together using 9 nuts and bolts. The distance between the anode and cathode was 2.0 cm while electrodes and the membrane was 1.0 cm. The current collectors were connected by external conducting wires to complete the circuit. A magnetic bar was inserted in the catholyte and stirred at a constant speed throughout the experiment. All the experiments were conducted at room temperature. Each labeled equipment in Figure 3.1 will be explained in the next subchapter.

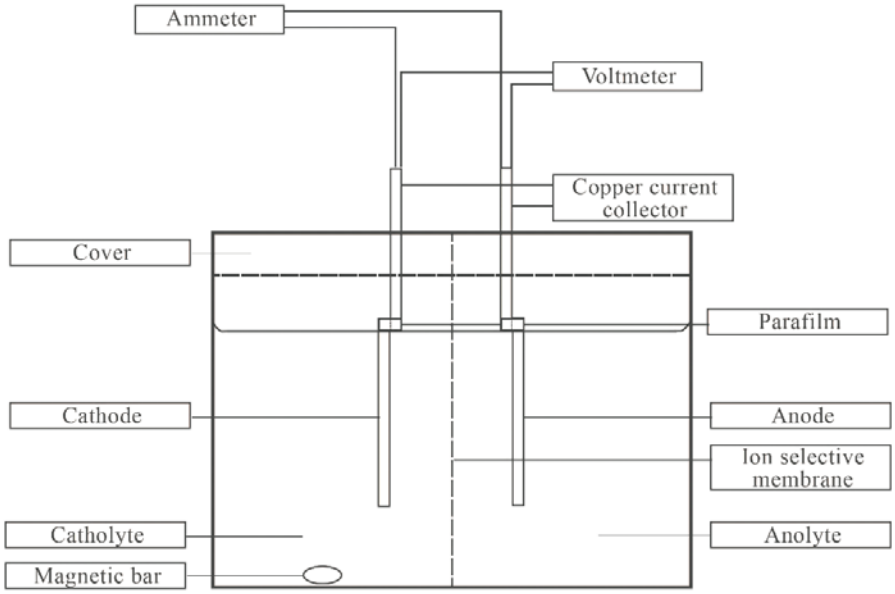


Figure 3.1 Schematic diagram of batch cell.

3.3 Types of equipment

3.3.1 Multimenter

A digital multimeter (Sanwa Electric Instrument Co) (Japan) was used as a measuring instrument (ammeter and voltmeter) during preliminary polarization studies and electrogenerative experiment. It can measure the output current (mA) and potential (mV).

3.3.2 Current collector

The copper plate was used as a current collector. It was wrapped around the junction of both anode and cathode with parafilm to prevent any contacts between the metallic surface and the electrolyte solution.

3.3.3 Electrodes

Two electrodes involved were anode and cathode. The cathode must undergo pretreatment before used and as for anodes, they were polished with sand paper before rinsed with distilled water and ethanol before used to ensure cleanliness of the surface. The details of the electrodes were presented in Table 3.1.

Table 3.1 Details of electrodes used.

Anode	**Cathode**
Zinc foil (2.0 cm × 4.5 cm × 0.05 cm) or Aluminum foil (2.0 cm × 4.5 cm × 0.05 cm)	RVC (2.0 cm × 4.5 cm × 0.3 cm), PG-25 (2.0 cm × 4.5 cm × 0.3 cm) or Stainless steel (2.0 cm × 4.5 cm × 0.1 cm)

3.3.4 Ion selective membrane

Ion selective or ion exchange membrane is a thin film of ion-exchange material used to separates ions in the electrolytes. The anion exchange membrane was used throughout the studies as a semi permeable separator which allows the transportation of anion charges between anolyte and catholyte compartment. An anion exchange membrane only allows negatively charged ion to move from anolyte to catholyte or vice versa. The membrane was cut into dimensions that fit the reactor and sandwiched between two rubber gaskets among the two compartments to prevent electrolyte leakage. After each experiment, the cell compartments were filled with distilled water to keep the moisture of the membrane.

3.3.5 Electrolyte

All the electrolytes were prepared from analytical grade reagents using distilled water. The catholyte was made up from a mixture of palladium(II) chloride in NaCl solution. The details of the experiment are shown in Table 3.2 and Table 3.3.

Table 3.2 Details of the electrolyte solution.

Anolyte	**Catholyte**
100 mL of 0.1 M NaCl	100 mL of 100 mg L^{-1} $PdCl_2$ in 0.2 M NaCl.

Table 3.3 Mass of Pd used in the experiment.

Compound	**Concentration (mg L^{-1})**	**Mass (g)**
$PdCl_2$	50	0.008
	100	0.017
	200	0.033
	500	0.083

3.3.6 pH meter

A pH meter (EUTECH Instrument) (USA) is used to measure the pH of the electrolytes. The pH of the solutions was between pH 3-6, measured using a pH meter. For other desired pH in this experiment, the solution pH was adjusted manually using 0.1 M HCl and 0.1 M NaOH.

3.3.7 Mechanical convection

A stirring hotplate (Favorit) (Malaysia) is used to enhance mechanical convection in the catholyte solution with scale 8. The presence of convection energy helps to improve mass transport in the deposition process (Terrazas-Rodríguez et al., 2011).